

DENTAL PRIMER VARNISH

The present invention relates to coupling agents which may be applied as primers or varnishes to dental substrate surfaces and which mediate improved adhesive bonding to resin-containing materials, such as composite dental filling materials.

In general, a varnish in dental materials may be defined as cavity liner which contains a resinous film-forming agent dissolved in an appropriate volatile solvent (F. A. Peyton, *Restorative Dental Materials*, 3d edition, Mosby, 1968, page 447). An appropriate solvent that may be used to dissolve the resin or polymers includes chloroform, alcohol, acetone, benzene, toluene, ethyl acetate, and amyl acetate.

Another author, R. W. Phillips, *The Science of Dental Materials*, 6th edition, Saunders, 1968, pages 510-511, lists as appropriate organic solvents acetone, chloroform, and ether, and these latter are preferred in the practice of the present invention, with acetone as most preferred.

The use and benefit of varnishes are that they may be placed under a restoration or filling to protect the cut dentinal tubules from the ingredients of the filling material and to assist in prevention of leakage of oral fluids under the restoration. In this invention, the varnish improves adhesive bonding between the tooth surface and the restorative material and thus acts as a coupling agent. This invention specially contemplates the utilization of chelate-forming adducts (addition-reaction products) in which N-phenylglycine or derivatives thereof, are reacted with each glycidyl ether where the reaction sites are the N-H group of the amino acid and each reactive epoxy group. The reaction occurs normally with slight heating over a 2-3 hour period, and the adhesive product or coupling agent is then preferably dissolved to about 5-15 percent by weight in acetone and utilized as a primer varnish to improve adhesion between a resin or composite material and human dentin or enamel.

PRIOR ART

The patent prior art relative to this invention is believed to be as follows:

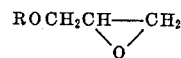
U.S. Pat. No. 3,200,142, Bowen. In this patent the coupling agent contained a chelate group similar to the present invention but also contained a polymerizable vinyl or methacrylate monomer group. However, the storage stability of solutions of the surface-active comonomer was lessened by virtue of the tendency of monomeric groups to polymerize during storage.

In the present invention it has been learned that there was sufficient dispersion-force interaction between the coupling agent and the overlying resin-containing dental material to produce significant adhesion even in the absence of copolymerizable groups. Thus, in the present invention, coupling agents containing in the same molecule an appropriate chelating group, together with a preferred aromatic moiety, have been found to give favorable adhesion. The compounds of the present invention have no monomer groups that can polymerize prematurely during storage as solutions and therefore convey greater storage stability capabilities adding to their present usefulness.

CHEMICAL VARIATION OF THE REACTANTS

With respect to the glycidyl ether-type compounds

providing the epoxy groups, there may be utilized glycidyl ethers providing monoepoxy, diepoxy, or polyepoxy groups, and the ethers of the present invention may be described according to the following formula:

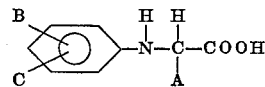


where R is a portion of the ether molecule more substantially described below. Where monoepoxies are utilized, a preferred ether is p-chlorophenyl glycidyl ether, and additional operable compounds include phenyl glycidyl ether and o-phenyl phenol glycidyl ether. Thus, in the formula above, for these compounds, respectively, R is p-chlorophenyl, phenyl and o-phenyl-phenyl.

Glycidyl ethers providing diepoxy groups may also be utilized in the present invention, and a preferred compound is the diglycidyl ether of bisphenol A, the diglycidyl ether of tetrachloro bisphenol A, and the glycerol diglycidyl ether (EPIOL G-100—Nippon), as well as the bisglycidyl ethers of chlorinated hydroquinone described in U.S. Pat. No. 2,682,547, Clemens et al. (Eastman) and the diglycidyl thio ethers of dithiols, U.S. Pat. No. 2,731,437, Bender (Carbide). Additionally, resorcinol diglycidyl ethers (ERE 1359—CIBA) may be utilized, as well as ethylene glycol diglycidyl ethers (EPIOL E-100—Nippon). Polyglycidyl reactants suitable for the present invention include tetraglycidoxytetraphenylethane (EPON 1031—Shell), as well as polyglycidyl ethers of novolac resins as exemplified under Union Carbide product ERR-0100 and the polyglycidyl ether of novolac polymers as exemplified by ECN 1325 and ECN 1299 CIBA.

Generally, the presence of a chloroaromatic, bromoaromatic, iodoaromatic, or polyaromatic group in the glycidyl ether moiety has been found to enhance the adhesive function of the final compound, whereas the presence of substantially aliphatic or fluorinated aliphatic moieties have the opposite effects.

As to the variation on the N-phenyl glycine reactant or fraction, the following have been found to be suitable variations of the basic N-phenyl glycine molecule as per the following formula:



where A = H, CH₃

B = H, CH₃, OCH₃, p-Cl phenoxy

C = H, CH₃

For example, preferred ring substituted aromatic glycines are N-(p-methoxy phenyl) glycine, N-[p-(p-chlorophenoxy) phenyl] glycine, and N-(3,5-dimethyl phenyl) glycine. Also operable are variations wherein the hydrogen on the α carbon of the glycine is replaced by methyl. It has been found further that substitution upward in the aliphatic series at α is deleterious due to steric hindrance.

The reaction products of the present invention may be compared favorably with natural materials such as copalite, a natural resin which has previously been used as a cavity varnish and is discussed in Peyton, ante, page 256, column 2.